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Baar, Hein J.W. de; Saager, Paul M.; Nolting, Rob F.; Meer, Jaap van der

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Cadmium versus phosphate in the world ocean

Hein J.W. de Baar^{a,1}, Paul M. Saager^b, Rob F. Nolting^a, Jaap van der Meer^a

^a*Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Den Burg (Texel), The Netherlands*

^b*Department of Earth Sciences, Free University, de Boelelaan 1085, 1081 HV Amsterdam, The Netherlands*

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Abstract

Cadmium (Cd) is one of the best studied trace metals in seawater and at individual stations exhibits a more or less linear relation with phosphate. The compilation of all data from all oceans taken from over 30 different published sources into one global dataset yields only a broad scatterplot of Cd versus phosphate. However, the smaller high-quality dataset obtained by rigorous selection of only those stations with uniform Cd/PO₄-ratio in the deep waters, provides a consistent global description of the deep (> 1000 m) waters. The deep Cd/PO₄-ratio increases from about 0.18×10^{-3} in the subarctic North Atlantic to about $0.33\text{--}0.35 \times 10^{-3}$ in the northern Indian and Pacific Oceans, in accordance with increasing phosphate content, i.e. age, of the deep water. The increasing Cd/PO₄-ratio with age (and phosphate) of the deep water masses is a function of the coupling between biogeochemical cycling and deep water circulation. Changes in the latter, for example during a glacial period, inevitably lead to significant shifts in the Cd/PO₄ relationship of seawater.

There is a statistically significant bimodality of deep Atlantic versus deep Antarctic/Indo/Pacific waters, suggesting that the deep Atlantic is a distinct biogeochemical province for Cd cycling. This distinction is likely caused by the high inventories of both Cd and phosphate in Weddell Sea source waters. For each of both populations, a given concentration of phosphate yields a predicted value of Cd within ± 100 pM (Atlantic) and ± 200 pM (Antarctic/Indo/Pacific), respectively, at the 95% confidence level. If one ignores the bimodality, then for a given phosphate the corresponding Cd might be predicted within ± 150 pM at the 95% confidence level; the validity of this is currently being verified by studies of South Atlantic waters which may or may not provide the missing link between both populations.

Currently, the global distribution of the Cd/PO₄-ratio in surface, thermocline and deep waters is consistent with preferential biogeochemical removal of Cd versus phosphate from surface waters. The net result for Cd/PO₄ is not dissimilar to the preferential surface removal of ¹²C over ¹³C driving the deep distribution of the dissolved ¹²C/¹³C-ratio, although for Cd/PO₄ the underlying mechanism is obviously very different and not well understood.

1. Introduction

The vertical profiles of Cd reported in 1976 (Boyle et al., 1976; Martin et al., 1976) were

among the first convincing concentration values for transition metals in ocean waters. Throughout the water-column, a remarkable correlation with nutrients phosphate or nitrate was found, indicative of an involvement of Cd in the marine biological cycle. Since then, several more vertical profiles of Cd and other transition metals have

¹Corresponding author. Telephone: 31 2220 69465. Telefax: 31 2220 19674. Omnet: NIOZ.TEXEL.

been reported to exhibit more (e.g. Cd, Zn) or less (e.g. Ni, Cu, the lanthanides) correlation with nutrient elements phosphate/nitrate as well as silicate (Bruland, 1983). In contrast with for example the group IV elements Ge and Si (Froelich et al., 1989) or the group IIIa lanthanide series (De Baar et al., 1991) there is no a priori reason for expecting a substantial relationship between elements Cd (group IIa) and P (group V). From linear regression of the first datasets (Boyle et al., 1976; Bruland et al., 1978; Bruland, 1980; Bruland and Franks, 1983) it appeared that the slope of Cd to phosphate varied within a fairly narrow (~ 0.25 to $\sim 0.4 \times 10^{-3}$) range, whereas the zero-phosphate intercept was generally near ($-0.1 \text{ nM} < \text{Cd} < 0.1 \text{ nM}$) the zero-Cd.

In an early compilation (Hester and Boyle, 1982) a linear relation with zero intercept was suggested, with a slope (in this case also the ratio) of Cd versus phosphate being 0.35×10^{-3} (as mentioned in Boyle, 1988). Shortly afterwards, the regression of Cd and phosphate in deep North Atlantic waters was found to yield a slope about 15% lower than in deep North Pacific waters (Bruland and Franks, 1983).

At about 1986–1987, Cd–PO₄ data had been published in some fifteen different articles, albeit almost exclusively for Northern Hemisphere stations. From this only seven datasets were selected without specification of selection criteria (Boyle, 1988). One large unpublished eastern Atlantic dataset had been added, but in retrospect is to be rejected due to poor phosphate data (Burton, pers. commun., 1993). Two other datasets, albeit excellent, were from a shallow inshore site off Gibraltar (Boyle et al., 1985) and the semi-enclosed Gulf of Mexico (Boyle et al., 1984). Otherwise, upon excluding surface-water values [above which depth(s) was not specified], the eight datasets had been combined into one plot (Boyle, 1988, fig. 1), as said based only on Northern Hemisphere stations (the southernmost being just north of the equator at 00°04'N, 13°14'W; Statham, 1984, unpubl. results due to faulty phosphate data). Despite this regional limitation, the Cd–PO₄ relationship was reported to be remarkably uniform globally. Furthermore, there was a presumed shift in the relation at about 1.3 μM

phosphate and two separate relations had been proposed:

$$\text{Cd} = -0.25 + (0.4 \times 10^{-3}) \times \text{PO}_4 \quad (1)$$

(Boyle, 1988) for PO₄ > 1.3 μM , i.e. largely North Pacific deep waters and

$$\text{Cd} = (0.2 \times 10^{-3}) \times \text{PO}_4 \quad (2)$$

(Boyle, 1988) with virtually zero intercept for PO₄ < 1.3 μM , i.e. all upper ocean waters (except the mixed layer) and almost all North Atlantic deep waters. The first relation (1) is dominated by deep North Pacific values [Boyle (1988) also mentioned South Atlantic but we failed to find any such site in the data]. Its apparent linearity is appealing, but the large non-zero intercept is not consistent with ideal covariation (Fanning, 1992). When expressed as the ratio Cd/PO₄:

$$\text{Cd}/\text{PO}_4 = (-0.25)/\text{PO}_4 + (0.4 \times 10^{-3}) \quad (3)$$

it is obvious that this ratio tends to increase with increasing [PO₄] in a non-linear fashion. Currently these regressions have become obsolete as they hinged strongly on the now rejected large east Atlantic dataset (concentric squares in fig. 1 of Boyle, 1988). It is also questionable whether the stations off Gibraltar and in the Gulf of Mexico are truly representative for deep water oceanography, where on the other hand some other published data (e.g. Danielsson et al., 1985, among others) had not been taken into account.

Recently, several new datasets have become available, most notably alleviating the paucity of data for the Indian Ocean (Saager et al., 1992), the South Pacific Ocean (Hunter and Ho, 1991) and the Antarctic Circumpolar Current, representative for the Southern Ocean (Martin et al., 1990; Nolting et al., 1991). This allows an assessment of the global marine geochemistry of Cd from its worldwide relationship with phosphate. Here, we are relying on the complete world data set derived from all available (over thirty) published sources as well as some additional new data of ourselves. First, we briefly assess the hitherto common practice of linear regression at each individual station. This provides some regional insight but can be misleading and does not yield any consistent global description either. Next, the Cd/PO₄-ratio

as function of depth has been plotted for each station in order to apply a well-specified selection criterion based on uniformity of this ratio in deep waters. This allows proper selection of a smaller high-quality dataset which for the first time provides the consistent, statistically documented, as well as truly global description of the deep (> 1000 m) waters. Subsequently, the signature and role of source and bottom waters is shown. Finally, the underlying biogeochemical processes as well as paleoceanographic implications are discussed.

2. Regional trends

For each published dataset the relationship between Cd and phosphate has usually been reported for the complete vertical water column at each station (Table 1). Excluded were shallow inshore stations, semi-enclosed basins (Gulf of Mexico, Mediterranean, Weddell Sea) and surface water transects. At some stations we noticed a tendency for Cd in surface waters to deviate from the overall linear relation, yet the relations reported here are for the whole water column (except for the distinct break in our own northwest Indian Ocean data; Saager et al., 1992).

In the Arctic waters of the Atlantic Ocean, the relatively low concentrations of Cd and phosphate are accompanied by a Cd/PO₄ slope which is generally low ($0.12\text{--}0.16 \times 10^{-3}$, not unlike commonly observed in oceanic surface waters) with a zero-phosphate intercept of Cd ≈ 0.065 nM. In one instance, no correlation was found at all (Danielsson et al., 1985). In the temperate zone of the northeast Atlantic basin the Cd/PO₄ slopes appear very uniform at about 0.19×10^{-3} where intercepts are variable from -0.021 to $+0.041$ nM. Our results of four 1989 and 1990 JGOFS (Joint Global Ocean Flux Study, North Atlantic Experiment) profiles fit in with earlier reported datasets (Table 1). In the northwestern Atlantic Ocean, the Cd/PO₄ slope appears to be slightly higher and more variable ($0.18\text{--}0.28 \times 10^{-3}$) with intercepts ranging from -0.019 to $+0.041$ nM. Our equatorial Atlantic station off Zaire (Nolting et al., unpubl.) exhibits a similar slope (0.22×10^{-3}) with

a slightly more pronounced negative intercept (-0.083 nM). In general the zero-phosphate intercepts are quite small.

For the northwestern Indian Ocean, the correlation of Cd with phosphate shows a distinct break between surface and deep waters (Saager et al., 1992). The Cd/PO₄ slope was low at about 0.15×10^{-3} in surface waters, but very high at 0.50×10^{-3} and 0.87×10^{-3} in deep waters at an offshore station and an inshore station, respectively. The latter was located in the upwelling area near Oman. The intercepts were quite negative at -0.49 nM and -1.26 nM at the offshore and inshore station, respectively. In the southeast Indian Ocean (Nolting et al., 1989) one station exhibits a slope of 0.19×10^{-3} with an intercept of 0.047 nM.

In the Southern Ocean, the very high Cd/PO₄ slopes of about 0.64×10^{-3} for several stations (Martin et al., 1990; Nolting et al., 1991) are consistent with the slope of 0.58×10^{-3} which was found when plotting the data for the first available South Pacific station on its own (Table 1), rather than combined with North Pacific sites (Boyle et al., 1976). In fact, this station is very near Antarctic waters. Both in the Southern Ocean and at this South Pacific station (south of New Zealand), the zero-phosphate intercept is distinctly negative (-0.85 to -0.41 nM). Such a combination of high slopes and distinctly negative intercepts was also found in the northwest Indian Ocean (see above).

The only other data for the South Pacific were for the marginal slope and shelf region at $35\text{--}40^\circ\text{S}$, just west off the Northern tip of New Zealand (Hunter and Ho, 1991). The deepest stations reach until about 1800 m. At these stations, the Cd/PO₄ slopes ($0.25\text{--}0.31 \times 10^{-3}$) with low zero-phosphate intercepts are intermediate between the North Atlantic and North Pacific Oceans. Yet recently, Frew and Hunter (1992) reported low Cd/PO₄ ratios for a South Pacific station ($48^\circ 05'\text{S}$, $164^\circ 30'\text{E}$). This is northwards of the Southern Ocean proper for which the authors believed no data was available (between 48 and 60°S) where in fact Cd–PO₄ data had been published previously (Westerlund and Öhman, 1991; Nolting et al., 1991, and references therein). It

Table 1

The relation between Cd [nM] and orthophosphate [μ M] in the world ocean for vertical profiles of all published stations currently available

Region	Latitude	Longitude	Cd[nM] = $aP[\mu\text{M}] + b$		r	n	Depth range	References
			a	b				
Arctic Ocean								
Arctic Atlantic	82.31°N	43.57°E	0.14	0.075		10	0–2400	Danielsson and Westerlund (1983)
N NE Atlantic	67°N	2°W	0.16	0.04		10	0–4000	Nolting et al. (1987)
N NE Atlantic	65.00°N	1.00°W	(no correlation was found)			8	0–2800	Danielsson et al. (1985)
	59.00°N	20.00°W	0.12	0.08	0.94	8	0–2800	Danielsson et al. (1985)
Atlantic Ocean								
NE Atlantic	~ 50°N	~ 20°W	0.19	0.001	0.96	22	0–3500	Danielsson et al. (1985)
	(4 stations)							
NE Atlantic	48.30°N	20.00°W	0.20	–0.004	0.98	8	0–2700	Danielsson et al. (1985)
NE Atlantic	33°N	20°W	0.211	0.037	0.96	10	0–2500	JGOFS (25 September 1989; PMS, Amsterdam)
NE Atlantic	33°N	20°W	0.200	–0.003	0.98	24	0–4400	JGOFS (27 April 1990; RFN-NIOZ)
NE Atlantic	58.3N	20.3W	0.182	–0.006	0.90	19	0–3000	JGOFS (4 June 1990; PMS, Amsterdam)
NE Atlantic	47°N	20°W	0.206	–0.005	0.96	18	0–4500	JGOFS (10 June 1990; PMS-A'dam)
NE Atlantic	39.22°N	12.51°W	(no values reported)					Statham et al. (1985)
(their station 10704 with Cd concentrations similar to other NE Atlantic data)								
Off Gibraltar	36°N	7°W	0.206	0.009	0.978	18	0–730	Boyle et al. (1985)
(fine dataset yet at shallow inshore station, not used in this paper)								
NW Atlantic	34.06°N	66.07°W	0.25	–0.019	0.995	11	0–2962	Bruland and Franks (1983)
NW Atlantic	~ 40°N	~ 65°W	0.18	0.023	0.908	49	0–2000	Sakamoto-Arnold et al. (1987)
	(~ 4 stations)							
WCR 82-B	36.38°N	73.47°W	0.18	0.041	0.961	21	0–2005	Sakamoto-Arnold et al. (1987)
Sargasso Sea	35.39°N	71.53°W	0.21	0.005	0.991	19	0–3000	Sakamoto-Arnold et al. (1987)
NW Atlantic	~ 50.0°N	~ 50.0°W	0.28	–0.03	0.809	55	0–4310	Yeats and Campbell (1983)
	(3 stations)							
NW Atlantic	~ 60.30°N	~ 17.0°W	0.26	0.016	0.95	11	0–2400	Olafsson (1983)
NW Atlantic	50°N	17°W	0.26	0.02		11	0–5000	Nolting et al. (1987)
Gulf of Mexico	24.1°N	84.5°W	0.257	0.04	0.996	10	100–3390	Boyle et al. (1984)
(fine data but semi-enclosed basin, not used in this paper)								
Equatorial								
Atlantic (Zaire)	6.30°S	8.19°E	0.22	–0.083	0.88	12	0–4000	Nolting et al. (unpubl.)
Southern Ocean								
Antarctic Atlantic	57°S	49°W	0.63	–0.76	0.91	30	0–4000	Nolting et al. (1991)
Antarctic Atlantic	67°S	28 > °E	(no relation was found; $r < 0.03$)					Orren and Monteiro (1985)
Drake Passage	60.46°S	63.26°W	0.65	–0.85	0.986	10	0–1850	Martin et al. (1990)
Antarctic								
Indian Ocean	54.40°S	63.06°E	0.68		0.801	8	0–3346	Bordin et al.(1987)
	61.05°S	66.20°E	0.82		0.775	8	0–3551	Bordin et al.(1987)
Indian Ocean								
SE Indian Ocean	10.70°S	112.0°E	0.19	0.047	0.954	8	0–3500	Nolting et al. (1989)
NW Indian Ocean	14.30°N	67.00°E	0.50	–0.49	0.97	14	100–4000	Saager et al. (1992)
	14.30°N	67.00°E	0.15	–0.054	0.999	4	0–100	Saager et al. (1992)
NW Indian Ocean								
Upwelling	22.30°N	60.40°E	0.87	–1.26	0.96	10	50–3000	Saager et al. (1992)
	22.30°E	60.40°E	0.16	–0.014	0.97	5	0–50	Saager et al. (1992)

Table 1 (Continued)

Region	Latitude	Longitude	Cd[nM] = $aP[\mu\text{M}] + b$		r	n	Depth range	References
			a	b				
South Pacific Ocean								
SW Pacific (Geosecs 293)	52.50°S	178.05°W	0.581	−0.41	0.879	19	0–5271	Boyle et al.(1976)
Tasman Sea	34.30°S	171.42°E	0.38	−0.001	0.97	11	0–866	Hunter and Ho (1991)
	35.50°S	162.40°E	0.29	−0.05	0.95	22	0–1793	Hunter and Ho (1991)
Puyseger Tr.	48.05°S	164.30°E	0.351	−0.237	0.98	34	25–4450	Frew and Hunter (1992)
North Pacific Ocean								
NE Pacific	~ 35°N	~ 130°W	0.35	−0.068	0.992	34	0–5000	Bruland (1980)
	(3 stations)							
NE Pacific			0.27	−0.048	0.957	35		Martin et al., (1976)
NE Pacific			0.36	−0.037				Knauer and Martin (1981)
NE Pacific	30.34°N	170.36°E	0.28	0.054	0.935	21	0–5446	Boyle et al., (1976)
NE Pacific	~ 47°N	~ 130°W	0.23	−0.042	0.941	21	0–3000	Jones and Murray (1984)
	(2 offshore stations)							
NE Pacific	~ 47°N	~ 126°E	0.36	0.039	0.918	17	0–2000	Jones and Murray (1984)
	(2 inshore stations)							
NE Pacific	50°N	145°W	0.35	0.048	0.974	21	0–4000	Martin et al. (1989)
(VERTEX VII at station Papa)								
N. Pacific			0.32	0.028	0.995	27	0–2000	Martin et al. (1985, pers. commun., 1986)
(VERTEX IV)								
NW Pacific	33.56°N	143.23°E	0.33	0.023	0.961	24	0–2000	Matsunaga and Abe (1985)
	42.29°N	155.00°E	0.29	0.011	0.938	11	0–600	Matsunaga and Abe (1985)

Overall database available upon request from first author (HJWdB). Slope Cd/PO₄ is a ; intercept is b ; r is coefficient of correlation for n number of datapoints. Data over complete depth range, except as indicated. Some publications do not contain the actual data of either Cd and/or phosphate, in such case the published linear relation is given, in some instances only reported for the combined datasets of 2–4 stations within one area. Nitrate values reported by Bordin et al. (1987) were converted to phosphate using the 1/16 Redfield-ratio. Unfortunate omissions of values of latitude, longitude, r and n reflect similar omissions in the original publications. Earlier Indian Ocean deep-water values (Danielsson, 1980) agree well with our recent estimates (above at 14.30°N, 67°E; Saager et al., 1992) but grouped relations for several stations cannot be resolved as phosphate not reported. Data taken from given references. Our JGOFS data reports available from the authors. Unpublished Cd values of Vertex IV by pers. commun. (1986), samples were collected as in Martin et al. (1985). Excluded were shallow and/or inshore stations (Martin et al., 1976; Boyle et al., 1985; Yeats and Westerlund, 1991) semi-enclosed basins (Boyle et al., 1984, 1985; Statham et al., 1985; Westerlund and Öhman, 1991), surface-water sections (Boyle et al., 1981; Kremling and Pohl, 1990) and Antarctic values of Orren and Monteiro (1985). The unpublished East Atlantic values of Statham and Burton as used in fig. 1 of Boyle (1988) in retrospect suffer from phosphate data being unreliable (Burton, pers. commun., 1993) and are here ignored. Data off New Zealand (Frew and Hunter, 1992) listed but not used as phosphate values appear too high. Data off Gibraltar (Boyle et al., 1985) and in Gulf of Mexico (Boyle et al., 1984) is listed (was also shown by Boyle, 1988, fig. 1) but not used in this paper as being from shallow inshore and semi-enclosed basin sites, respectively.

was suggested that the low Cd/PO₄ ratio at their station was a clear signal of Antarctic Intermediate Water (AAIW) and that Antarctic and Sub-Antarctic waters are influenced by a common process that generates such low ratios. For the upper water column of the Antarctic Ocean proper, such low ratios had indeed already been reported (Nolting et al., 1991). Surface waters virtually always show lower Cd/PO₄ ratios than deep waters. Otherwise

the phosphate values as reported appear about 10% higher than at nearby Geosecs stations. This would explain the rather low Cd/PO₄ ratios as reported and upon correction largely nullify the perceived influence of Southern Ocean waters on the Cd–PO₄ properties of the global ocean (Frew and Hunter, 1992).

The more abundant datasets for the North Pacific Ocean generally reveal a higher Cd/PO₄ slope

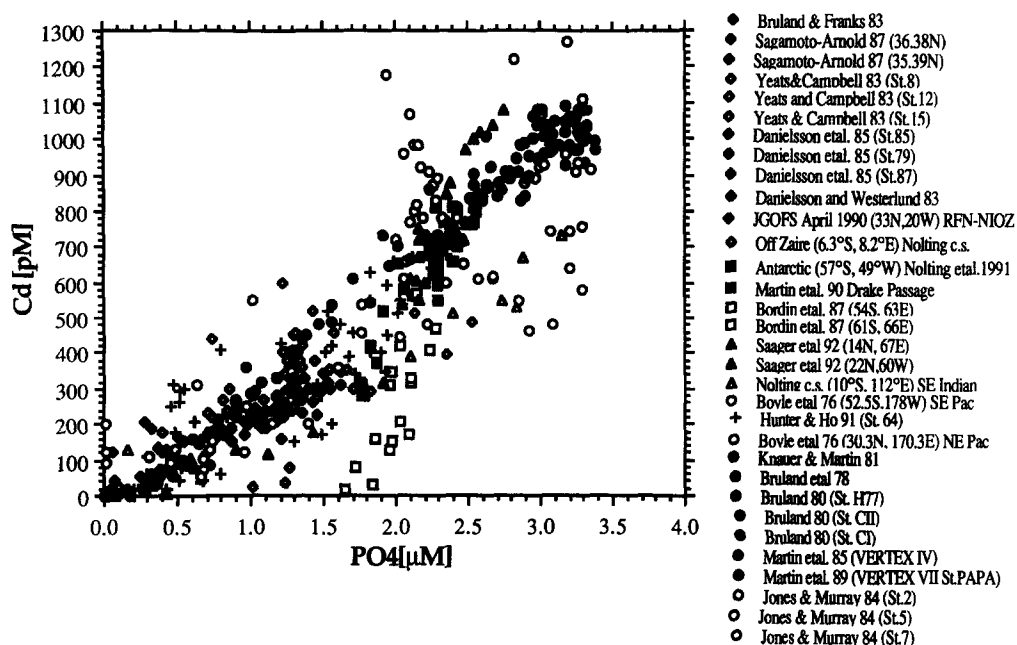


Fig. 1. All available oceanic Cd values [pM] plotted versus corresponding phosphate concentrations [μM]. Pacific as circles, Atlantic as diamonds, Antarctic as squares, Indian Ocean as triangles. Datasets for which the deep values fall within the selection criterion for deep waters [$\text{SD}(\text{Cd}/\text{PO}_4) < 10\%$] are presented as filled symbols, but note that all such data are plotted, i.e. including surface waters. All open symbols represent datasets outside this criterion. Crosses represent southeast Pacific dataset of Hunter and Ho (1991) which cannot be subjected to this criterion.

than in the northeast Atlantic Ocean, intercepts are quite modest from -0.068 to $+0.054$ nM. No clear distinction can be made between the western and eastern North Pacific regions. Remarkably, in one study of the northeast Pacific (Jones and Murray, 1984) two offshore stations exhibited a lower Cd/ PO_4 slope (0.23×10^{-3}) as compared to two inshore stations (0.36×10^{-3}).

Correlating of properties along a vertical profile, intersecting various distinct water masses, is to be viewed with caution. Notably at stations from several publications, the significant coefficient of correlation results at least partly from the fact that a cluster of near-zero surface water values was combined with a cluster of high deep water values. Combination of such non-Gaussian populations into one linear regression is questionable. In the Southern Ocean one finds the opposite. Here, high levels of nutrients (i.e. phosphate) and Cd are maintained also in the surface waters (Nolting et al., 1991), in other words the near-zero endmember is missing and the overall coefficient of correlation

at first glance appears less significant than in the oligotrophic gyres of the temperate zones (Table 1). Summarizing, the compilation of regional slopes and non-zero intercepts provides some clues, but does not yield a distinct worldwide relation.

3. Towards a global description

Combination of all currently available data into one plot (Fig. 1) shows a broad trend of Cd versus phosphate. Upon rejecting outliers (open symbols for stations where the deep water Cd/ PO_4 ratio has a mean value with standard deviation exceeding 15 percent, see below, section 4), the selected coherent data (filled symbols; for all depths, i.e. including surface waters) provides a quasi-linear trend throughout the water column of all oceans. The gap in the $\sim 1.5 < \text{PO}_4 < \sim 2.0$ interval is due to the virtual absence of data from temperate zones in the Southern Hemisphere. This gap is somewhat filled by one southeast Pacific dataset (Hunter

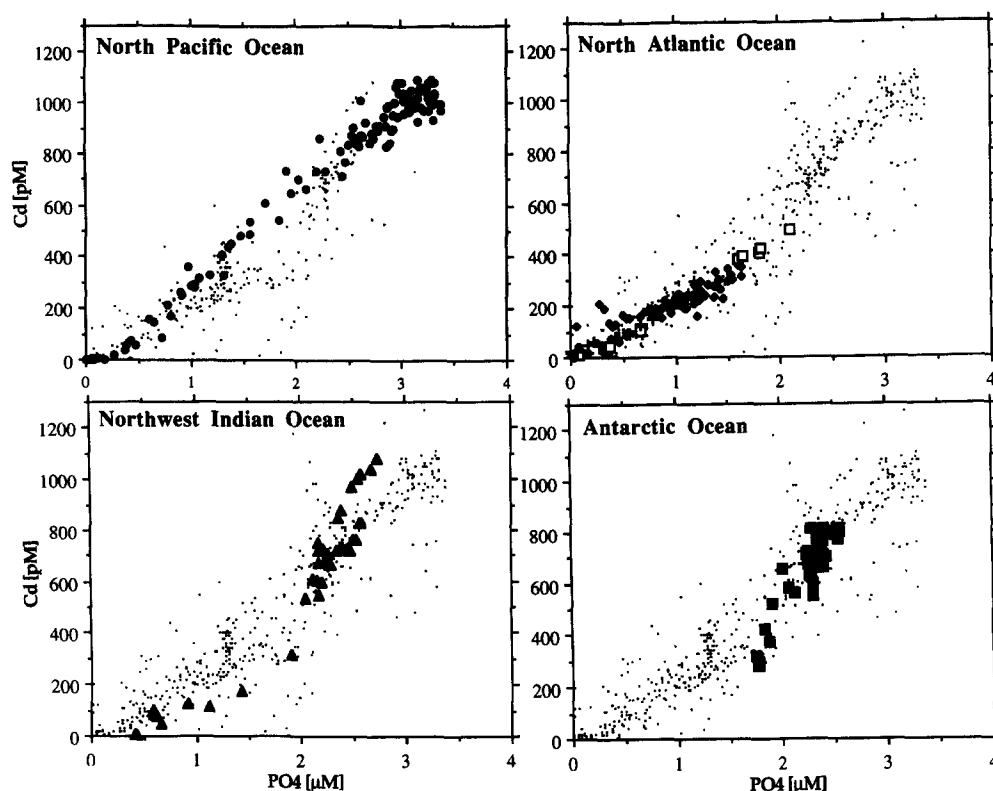


Fig. 2. The datasets of Cd [pM] versus phosphate [μM] plotted for each ocean on its own, only the selected data is shown (filled symbols) following the criterion for the whole water column. Atlantic trend further supported with additional inshore station off Gibraltar (+) and a station in the semi-enclosed Gulf of Mexico (\square).

and Ho, 1991) which somehow escapes the outlier criterion and is therefore shown as crosses (Fig. 1).

Plotting the same data separately (Fig. 2) leaves us with strictly Northern Hemisphere stations for the Pacific Ocean, exhibiting remarkable linearity throughout the water column. At low $\text{PO}_4 < 0.2 \mu\text{M}$ in surface waters, there is no Cd detectable anymore, which indicates preferential removal of Cd versus phosphate. Linearity is also observed in the North Atlantic Ocean (\blacklozenge), further enhanced when illustrated with an inshore station near Gibraltar, as well as one station in the semi-enclosed Gulf of Mexico. The slope of this trend is below that of the Pacific Ocean in the same concentration range (Bruland and Franks, 1983). Notice also the lack of South Atlantic data. Finally the small datasets (filled symbols) for the Indian and Antarctic Oceans both exhibit their own unique trends. These waters, as well as the

Southern Hemisphere in general, are to be studied further.

4. The global description of deep waters

In order to arrive at a meaningful global description, it is better to ignore the upper ocean ($< 1000 \text{ m}$) and strictly rely on deep water distributions. This becomes obvious from plotting the molar Cd/ PO_4 ratio as a function of depth, as illustrated for four stations selected to represent the major ocean basins (Fig. 3). The vertical profile of the Cd/ PO_4 -ratio exhibits rapidly increasing values from the surface waters into the thermocline and uniformly higher values in deep waters, in fact resembling the individual profiles of Cd and PO_4 respectively, of which the ratio Cd/ PO_4 was derived. We plotted the depth profiles of Cd/ PO_4

Table 2

Averaged deep water concentrations of dissolved Cd, PO₄ and Cd/PO₄ ratio, including absolute and relative (for Cd/PO₄ in %) standard deviations

Latitude/ Longitude	References	<i>n</i>	Depth (m)	Cd (pM)	SD _{Cd}	PO ₄ (μM)	SD _{PO4}	Cd/P (pM/μM)	SD _{Cd/P}	%
Atlantic										
82.3°N, 43.6°E	Danielsson and Westerlund, 1983	5	600–3400	202	12.8	0.88	0.10	231	21.3	9.2
65°N, 1°W	Danielsson et al., 1985	4	500–2000	195	5.8	1.07	0.02	182	9.4	5.2
59°N, 20°W	Danielsson et al., 1985	4	500–2000	230	16.3	1.21	0.11	190	16.2	8.5
48.3°N, 20°W	Danielsson et al., 1985	5	1000–2700	253	30.1	1.25	0.05	202	19.0	9.4
35.4°N, 71.5°W	Sakamoto-Arnold et al., 1987	7	850–3000	245	22.0	1.16	0.13	212	10.0	4.7
36.4°N, 73.5°W	Sakamoto-Arnold et al., 1987	9	350–2000	274	26.1	1.27	0.10	215	13.5	6.3
34°N, 66°W	Bruland and Franks, 1983	5	1000–2960	286	29.3	1.23	0.08	233	11.5	4.9
33°N, 20°W	JGOFS (25 September 1989; PMS, Amsterdam)	4	1200–2500	205	35.0	1.23	0.07	166	18.5	11.1
33°N, 20°W	JGOFS (27 April 1990, RFN, NIOZ)	11	1500–4500	293	47.3	1.47	0.14	198	18.9	9.6
58.30°N, 20.30°W	JGOFS (4 June 1990, PMS, Amsterdam)	7	800–2500	233	6.3	1.23	0.04	195	16.5	8.5
47°N, 20°W	JGOFS (10 June 1990, PMS, Amsterdam)	7	1000–4500	287	42.9	1.39	0.15	205	12.2	5.9
53°N, 50°W	Yeats and Campbell, 1983	18	191–3550	334	45.7	1.29	0.03	259	36.9	14.2
50°N, 50°W	Yeats and Campbell, 1983	11	500–4200	361	49.2	1.30	0.05	278	37.9	13.6
45°N, 50°W	Yeats and Campbell, 1983	16	500–4310	392	94.0	1.33	0.08	296	73.4	26.8
6.3°S, 8.2°E	Nolting et al. (unpubl.)	7	500–4000	385	88.2	1.96	0.38	197	31.5	16.0
<i>Off Gibraltar</i>										
36°N, 7°W	Boyle et al., 1985	7	450–730	(226)	(33.9)	(1.03)	(0.10)	(218)	(15.7)	(7.2)
<i>Gulf of Mexico</i>										
24.1°N, 84.5°W	Boyle et al. 1984	4	1000–3390	(400)	(15.5)	(1.71)	(0.10)	(234)	(5.9)	(2.5)
Antarctic										
57°S, 49°W	Nolting et al., 1991	23	300–4000	691	71.2	2.29	0.09	299	27.4	9.2
60.5°S, 63.3°W	Martin et al., 1990	7	200–1850	735	62	2.45	0.10	300	16.0	5.3
Indian										
14.3°N, 67°E	Saager et al., 1992	10	700–4000	736	67	2.41	0.15	305	15.7	5.1
22.3°N, 60.4°E	Saager et al., 1992	5	800–3000	1004	75.4	2.59	0.13	388	11.2	2.9
10.7°S, 112°E	Nolting et al., 1989	4	750–2500	620	95.9	2.75	0.36	213	23.0	10.8
Pacific										
30°N, 170°W	Boyle et al., 1976	12	900–5500	794	152.0	2.68	0.28	295	40.8	13.8
53°N, 170°W	Boyle et al., 1976	13	500–3700	1066	59.5	2.93	0.09	363	16.4	4.5
52.5°S, 178°W	Boyle et al., 1976	14	1100–5200	854	128.0	2.14	0.08	397	59.7	15.0
~ 36°S, ~ 164°E	Hunter and Ho, 1991	20	1083–1793	(650)	(84.3)	(2.20)	(0.22)	(296)	(19.6)	(6.6)
48.05°S 164.30°E	Frew and Hunter, 1992	19	1000–4450	595	58	(2.34)	(0.124)	(254)	(15.5)	(6.1)
37°N, 123.5°W	Bruland et al., 1978	7	600–2500	914	93.5	3.12	0.22	301	15.4	5.1
32.4°N, 145°W	Bruland, 1980	10	800–4800	895	87.2	2.79	0.31	322	14.9	4.6
37°N, 124°W	Bruland, 1980	11	490–3900	973	78.5	3.03	0.22	322	10.3	3.2
36.5°N, 122.5°W	Bruland, 1980	7	580–2250	996	74.5	3.04	0.14	326	10.7	3.3
36.5°N, 123°W	Knauer and Martin, 1981	5	500–2000	1078	10.9	3.09	0.15	349	15.0	4.3
28°N, 155°W	Martin et al., 1985	12	700–2200	1021	35.8	3.25	0.12	314	16.7	5.3
50°N, 145°W	Martin et al., 1989	14	300–4000	948	62.2	2.90	0.20	328	9.6	2.9
47°N, 126°W (st. 2)	Jones and Murray, 1984	4	400–1200	1062	163.0	3.23	0.06	329	51.8	15.7
47°N, 130°W (st. 5)	Jones and Murray, 1984	6	600–3000	657	113.0	3.09	0.17	209	31.6	15.1
47°N, 130°W (st. 7)	Jones and Murray, 1984	4	600–1600	742	204.0	3.26	0.12	222	66.0	29.7

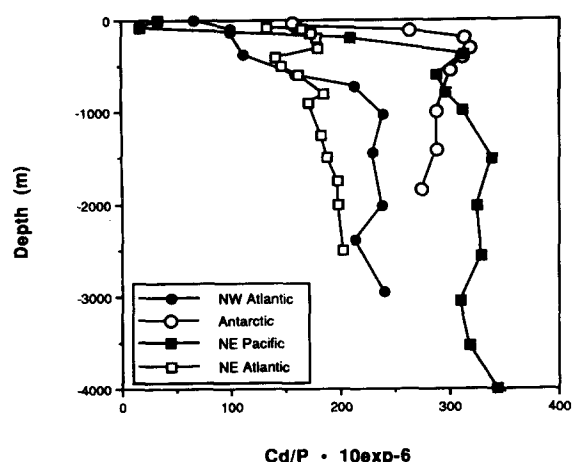


Fig. 3. Examples of the vertical distribution of the ratio Cd/PO_4 [$\text{pM}/\mu\text{M}$] at selected stations in the North East Atlantic (JGOFS), northwest Atlantic (Bruland and Franks, 1983), Antarctic (Martin et al., 1991) and northeast Pacific (Bruland, 1980) Oceans.

for all available datasets and found this to be the common trend at individual stations (not shown). Similar shifts in metal/nutrient ratio have also been found for other elements, e.g. Ni and Zn versus silicate (Saager et al., 1992). When removing the upper water column (< 1000 m) from the dataset, we also remove the very surface waters. There, levels of Cd and phosphate often are very low, for some stations near the detection limit, so that for some (but not necessarily all) datasets the precision is not as good as for deeper waters. As a matter of fact the same applies for global assessment of the nutrients nitrate and phosphate (Fanning, 1992). By removing the surface waters data, the precision of the remaining dataset as used below would therefore have improved.

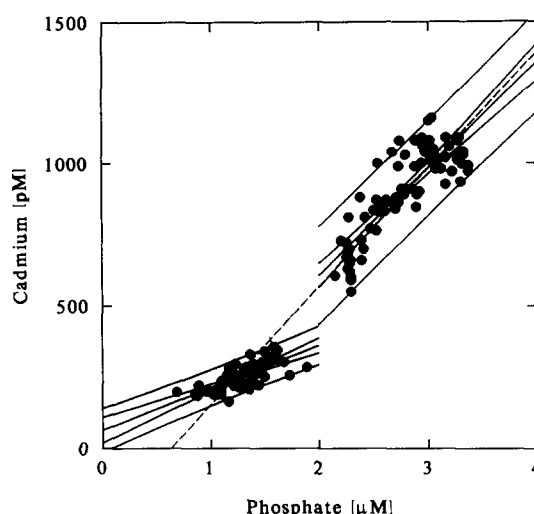


Fig. 4. The individual datapoints of deep (> 1000 m) water Cd [pM] at selected stations [$\text{SD}(\text{Cd}/\text{PO}_4) < 10\%$] plotted versus deep water concentration of phosphate [μM]. Two distinct clusters with separate linear regressions (middle lines) with 9% confidence intervals. (inner pairs of curves) Predictability intervals at 9% confidence level (outer pairs of lines) for predicting the band width of Cd from a given value of phosphate. Dotted line would represent one single linear regression of all datapoints. Recent values for the South Atlantic Ocean (Yeats, pers. commun., 1993) would tend to fill the gap between the two clusters, i.e. help justify the single dotted line regression. The recently reported South Pacific station of Frew and Hunter (1992) has not been plotted; however, upon downward adjustment of its phosphate values towards those of nearby Geosecs stations its deep values (> 1000 m) would have fitted the higher ($\text{PO}_4 > 2 \mu\text{M}$) cluster very well.

For many stations, the deep water value of Cd/PO_4 is very uniform (Fig. 3), yet for several other stations the ratio Cd/PO_4 in the deep water exhibited considerable scatter (Table 2). This is attributed to either natural variability or limita-

Depth criterion is defined as depth below the nutricline. After plotting the complete Cd/PO_4 -ratio vs. depth profile we selected those datapoints which are clearly below the maximum value of Cd/PO_4 , the latter typically situated at about 500–1000 m depth (see Fig. 4). For those datapoints we calculated the mean value and standard deviation. Datasets for which the standard deviation of the Cd/PO_4 ratio was less than 10% were selected for the plot in Fig. 4 of Cd vs. PO_4 for samples below 1000 m depth. Most stations of Hunter and Ho (1991) are unusual as they show both Cd and phosphate to increase regularly with depth, not unlike a typical silicate profile. The deep (> 1000 m) data of individual stations does not yield uniformity of the Cd/PO_4 -ratio. For illustration only the five stations (55, 57, 60, 62, 67) of Hunter and Ho (1991) were combined, then the Cd/P -ratio is fairly uniform with depth, however both Cd and PO_4 increase with depth, invalidating the above mean values which therefore are in brackets. Data off New Zealand (Frew and Hunter, 1992) not used as mean PO_4 at $2.34 \mu\text{M}$ appears too high; upon correction towards $\sim 2.14 \mu\text{M}$ at nearby Geosecs St. 280 the ensuing $\text{Cd}/\text{P} = \sim 278 \text{ pM}/\mu\text{M}$ would nicely fit the global trend. Inshore station off Gibraltar is shallow such that Cd and PO_4 only in upper ocean where both increase with depth, again invalidating their mean values therefore in brackets; also all data < 1000 m hence not used. Four datapoints in deep Gulf of Mexico not used as this is semi-enclosed basin.

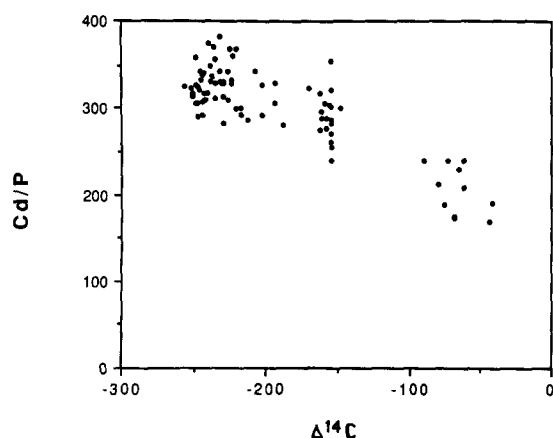


Fig. 5. Deep water ratio Cd/PO_4 [$\mu\text{M}/\mu\text{M}$] for individual samples at selected stations [for which $\text{SD}(\text{Cd}/\text{PO}_4) < 10\%$] plotted versus $\Delta^{14}\text{C}$ (‰) at nearby Geosecs stations (Ostlund et al., 1987).

tions of analytical reproducibility in the values of Cd and/or phosphate. Not being able to make a firm decision on either of the two latter options, we arbitrarily selected only those stations with very uniform deep water ratios of Cd/PO_4 , using a standard deviation of 10% as the criterion. The dataset thus obtained is undoubtedly of high quality, without necessarily suggesting that the rejected data is of poor analytical quality (Table 2).

Preferably, one would determine the Cd/PO_4 -ratio from relating Cd versus PO_4 of samples taken in well-defined deep water masses only, not unlike the treatment of phosphate versus other tracers within one coherent dataset (Broecker et al., 1985). This requires careful analysis of the hydrography at each station. However, most published Cd datasets are brief on hydrography. The pragmatic, admittedly less elegant, approach is to simply define all waters below 1000 m depth as definitely belonging to the deep thermohaline circulation, with the disadvantage of excluding some data from intermediate, yet still thermohaline driven, waters. In Fig. 4, the selected deep (> 1000 m) values are shown; note that for stations in the Arctic Atlantic Ocean and the Antarctic Circumpolar Current (Martin et al., 1990; Nolting et al., 1991) data from the whole water column were plotted. Both polar regions are exceptional as they provide the source waters for the deep oceans. The Southern Ocean (covering

about 10% of the world oceans) is exceptional also for another reason, namely that values of nutrients (i.e. PO_4) and Cd are very high in the surface waters (Nolting et al., 1991).

Some distinct groupings were found (Table 2; Fig. 4). The deep North Atlantic Ocean falls in a cluster with a typical Cd/PO_4 ratio of $\sim 0.2 \times 10^{-3}$ at about $1.2 \mu\text{M}$ phosphate. Deep waters of the North Pacific Ocean cluster around $\text{Cd}/\text{PO}_4 = \sim 0.33 \times 10^{-3}$ at $\text{PO}_4 = \sim 3.0 \mu\text{M}$. In other words, the older (lower $\Delta^{14}\text{C}$) North Pacific deep water has a Cd/PO_4 ratio some 65% higher than that of the North Atlantic deep water (Fig. 5). The deep waters of the Antarctic and Indian Oceans (Table 2), with intermediate age (and phosphate contents; Broecker et al., 1985) fall neatly in between North Atlantic and North Pacific deep waters (see also Fig. 5). The northwest Indian Ocean upwelling site exhibits a remarkably high Cd/PO_4 -ratio of 0.388×10^{-3} .

Clearly, more data would be desirable for other regions, yet the currently available distribution is obviously bimodal (Fig. 4). For linear regression ranking of the data according to estimated values yields an auto-correlation coefficient of 0.41 of the residuals, significantly ($P < 0.01$) different from zero. In other words, it would be inappropriate to describe the two dataclusters by a single linear relationship. In fact, the cluster of selected deep North Atlantic stations (all data with $\text{PO}_4 < 2 \mu\text{M}$) follows the relationship:

$$\text{Cd} = (0.065) + (0.148 \times 10^{-3}) \times \text{PO}_4 \quad r = 0.74 \quad (4)$$

suggesting lower ratios in analogy to the earlier relation (2). For the other cluster of high values ($\text{PO}_4 > 2 \mu\text{M}$ in Fig. 4), one finds:

$$\text{Cd} = (-0.145) + (0.375 \times 10^{-3}) \times \text{PO}_4 \quad r = 0.85 \quad (5)$$

This is remarkably consistent with the now obsolete relation (3) for the then used cluster of high values ($\text{PO}_4 > 1.3 \mu\text{M}$) in both thermocline and deep (mostly North Pacific) samples. Judging from the prediction intervals, a given phosphate

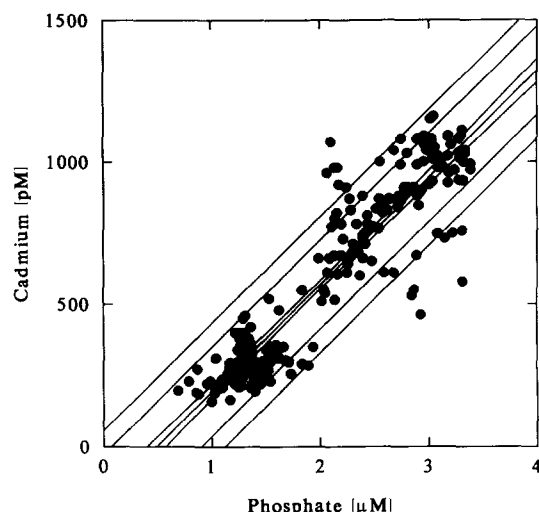


Fig. 6. Plot of Cd versus PO_4 for all (non-selected) individual samples for deep waters (> 1000 m) only. However, for the Arctic Atlantic Ocean all data from the whole water column was plotted. Linear regression (middle line) with 95% confidence interval. (curves). Predictability intervals at 95% and 80% confidence level, respectively (outermost and outer sets of lines) for predicting the band width of Cd from a given value of phosphate.

yields a predicted Cd with an uncertainty of about ± 100 pM in the deep Atlantic and about ± 200 pM in the Indo/Antarctic/Pacific at the 95% confidence level.

If, however, one ignores the bimodal distribution, then linear regression yields the overall relation:

$$\text{Cd} = (-0.259) + (0.413 \times 10^{-3}) \times \text{PO}_4 \quad r = 0.97 \quad (6)$$

akin to the above relations (3) and (5) for $\text{PO}_4 > 1.3 \mu\text{M}$ and $\text{PO}_4 > 2 \mu\text{M}$, respectively. For a given concentration of phosphate the corresponding Cd concentration then would be predicted with an uncertainty (not shown) of about ± 150 pM at the 95% confidence level (or ± 90 pM when satisfied with an 80% confidence).

Whether or not the current bimodality is a real oceanic feature, can only be assessed upon addition of intermediate datasets, most notably from the temperate Southern Hemisphere oceans for which virtually no data exists. For example, unpublished values of the South Atlantic Ocean (Yeats, pers.

commun., 1993) would tend to fill the gap. This is also true for the data off New Zealand (Hunter and Ho, 1991) which as mentioned escapes our outlier criterion.

Currently the bimodality is a fact, in oceanographic terms this would mean that the biogeochemistry and circulation of the Atlantic Ocean is distinct from that of the Indo/Pacific/Antarctic Oceans. This distinction might well be attributed to the additional strong signal (Cd as well as PO_4) of deep water formed in the Weddell Sea (see below, section 5).

For comparison, we also simply plotted all deep (> 1000 m) values as well as all polar values without any selection. Here, we find more spread in the data (Fig. 6) but otherwise the similar bimodal distribution with the relationship

$$\text{Cd} = (0.046) + (0.185 \times 10^{-3}) \times \text{PO}_4 \quad r = 0.706 \quad (7)$$

for $\text{PO}_4 < 2 \mu\text{M}$ and

$$\text{Cd} = (0.125) + (0.267 \times 10^{-3}) \times \text{PO}_4 \quad r = 0.625 \quad (8)$$

for the other cluster of high values ($\text{PO}_4 > 2 \mu\text{M}$). The recent observations of the Tasman Sea (Hunter and Ho, 1991) are unusual as they show a steady increase of both Cd and phosphate with depth. For this reason, they had dropped out of the earlier selected dataset (Fig. 4) but otherwise tend to fill the gap between the two data clusters (Fig. 5), illustrating the need for more Southern Hemisphere data. [Similarly the four deep samples (crossed squares in Fig. 2) from the semi-enclosed Gulf of Mexico would have helped bridging the gap].

For the overall dataset one would find:

$$\text{Cd} = (-0.137) + (0.356 \times 10^{-3}) \times \text{PO}_4 \quad r = 0.93 \quad (9)$$

In this case for a given concentration of phosphate the corresponding Cd concentration would be predictable with an uncertainty of about ± 210 pM at the 95% confidence level (Fig. 6). When satisfied

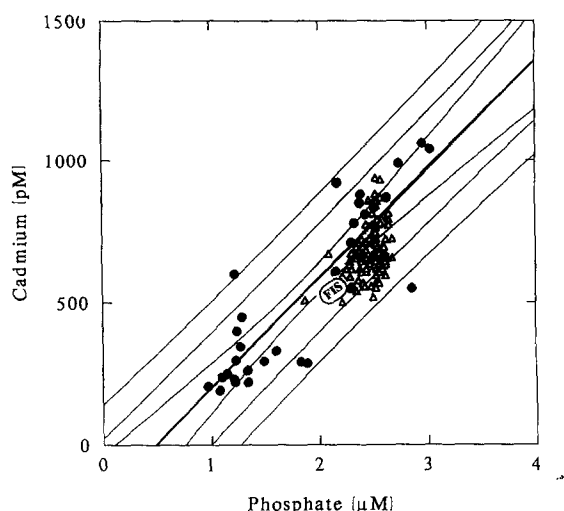


Fig. 7. Plot of Cd versus PO_4 for the deepest (bottom water) samples only at various oceanic stations (●) with linear regression (middle line). Linear regression with 95% confidence interval (curves). Predictability intervals at 95% and 80% confidence level, respectively (most outer and outer pairs of lines) for predicting the band width of Cd from a given value of phosphate. Shown for comparison is the additional dataset for the Weddell Sea of Nolting et al. (1991) and Westerlund and Öhman (1991) (△) as well as the FIS envelope of the Filchner Ice Shelf water data field of Westerlund and Öhman (1991).

with only 80% confidence the predictability is better at about ± 180 pM. Omission of the polar datasets (not shown) would yield:

$$\text{Cd} = (-0.183) + (0.376 \times 10^{-3})\text{PO}_4 \quad r = 0.92 \quad (10)$$

which does not deviate greatly from above relation (9). For a given concentration of phosphate, the corresponding Cd concentration would have an uncertainty of about ± 220 pM and ± 160 pM at the 95% and 80% confidence level, respectively.

5. Source and bottom waters

There is evidence that the Cd/Ca elemental ratio in shells of benthic foraminifera may reflect ambient PO_4 in today's bottom waters, with the underlying mechanism relying on the assumed Cd- PO_4 relation in these waters (Boyle, 1988). For this purpose, it would be adequate to define

the latter relation for bottom waters only. Of course, the overlying deep waters, through rapid lateral mixing along isopycnal surfaces, are also in contact with the seafloor benthic community, namely at the slope region of the ocean margins. Yet in section 4 above the deep waters were already included; here we restrict ourselves to abyssal bottom waters, with some reference to their source waters in the Weddell Sea and the northernmost North Atlantic Ocean.

When plotting only the deepest (bottom) sample for each station (Fig. 7), we find a reasonable relation with phosphate. For a given phosphate, the predictability of Cd is ± 270 pM and ± 170 pM at the 95% and 80% confidence level, respectively, i.e. far worse when compared with the above treatment of selected ($\text{SD} < 10\%$) deep water samples. Otherwise the corresponding Cd/ PO_4 ratio:

$$\text{Cd} = (-0.190) + (0.388 \times 10^{-3}) \times \text{PO}_4 \quad r = 0.88 \quad (11)$$

is akin to the ratio found in the other treatments of the global dataset (Eqs. 6, 9, 10).

Within the same graph we plotted the fields of values (Nolting et al., 1991; Westerlund and Öhman, 1991) for the southern source waters, that is the various water masses (Filchner Ice Shelf Water [FIS or ISW], Warm Deep Water [WDW], Antarctic Bottom Water [AABW], Weddell Deep Bottom Water [WDBW]) in the Weddell Sea. Mixing of ISW and upwelling WDW yields WDBW, which sinks to the bottom and, upon admixture with overlying AABW, eventually serves as the major southern source for the deep ocean circulation. In general, these Weddell Sea waters show highly variable relations of Cd and phosphate. For their complete dataset, Westerlund and Öhman (1991) reported the relation:

$$\text{Cd} = (-0.105) + (0.31 \times 10^{-3}) \times \text{PO}_4 \quad r = 0.58 \quad (12)$$

where the poor correlation illustrates the large variability. They mentioned that recalculation of the regression line with samples divided into different water masses or geographically (i.e. by station) does not give a better fit. When selecting only the

AABW data, Westerlund and Öhman (1991) could not discern a linear relation (Fig. 7). Despite the variability, the AABW can be viewed as a point source with $\text{Cd} = 0.7 \pm 0.2 \text{ nM}$, $\text{PO}_4 = 2.3 \pm 0.2 \text{ }\mu\text{M}$ and $\text{Cd}/\text{PO}_4 = \sim 0.3 \times 10^{-3}$.

Within the Circumpolar Current proper, these Weddell source waters mix with source waters of northern origin which contain much less (Atlantic), or similar (Indo/Pacific) levels of Cd and phosphate. The resulting deep water signals of both Cd ($0.7 \pm 0.07 \text{ nM}$) and PO_4 ($2.4 \pm 0.1 \text{ }\mu\text{M}$) become remarkably more uniform, judging from our deep station at 57°S , 49°W in the Circumpolar Current (Scotia Sea; Nolting et al., 1991 in Table 2; in keeping with the 200–1850 m interval of Martin et al., 1990 in Table 2). The absolute values of both Cd and phosphate in the Circumpolar Current appear compatible with a mixture consisting of about 45% Antarctic Bottom Water, 25% deep northern Atlantic and 30% intermediate Indo-Pacific waters, as previously assessed from the global Geosecs/TTO phosphate dataset (Broecker et al., 1985).

When eventually traveling northwards in the Pacific and Indian Oceans, these waters may receive a consistent Cd/PO_4 input from the continuous regenerative additions within those basins. This would, however, be relatively modest as the highest concentrations of Cd ($\sim 1.1 \text{ nM}$) and PO_4 ($\sim 3.5 \text{ }\mu\text{M}$) of oldest deep waters (Figs. 4, 6, 7) exceed the above levels ($\text{Cd} = 0.7 \text{ nM}$ and $\text{PO}_4 = 2.4 \text{ }\mu\text{M}$) in the deep Scotia Sea with only about 40%.

Similarly, we noticed earlier that the deep northern source waters of the (sub)Arctic Atlantic Ocean (north of the Scotland–Iceland–Greenland sills) commonly show little or no relation between Cd and PO_4 ; whenever a relation is discerned the ratio is usually low at about 0.2×10^{-3} (Table 2). Also, these northern source waters generally carry low levels of Cd and phosphate, in contrast with the southern (Weddell Sea) source waters. Hence, it might be argued that, due to these low levels, the northern source waters contribute little to the global inventory of Cd and PO_4 in bottom waters, this in contrast with the Weddell Sea source term. With respect to the Cd/PO_4 -ratio this implies that the deep Atlantic basin is a distinct province, well dis-

tinguished from the Cd/PO_4 -ratio in other basins due to the strong Weddell Sea contribution.

6. Biogeochemical cycling of Cd versus phosphate

There are different, and evolving, perspectives on the true nature of ocean circulation, on the mechanisms of biogeochemical cycling and, last but not least, on the proper statistical treatment of field observations. Nevertheless, the above approach strongly suggests that the Cd/PO_4 ratio increases with the age of the deep water (Fig. 5).

For the apparent fractionation of Cd versus PO_4 several mechanisms can be envisioned. Firstly, the microplankton in surface waters may accumulate and remove Cd more efficiently than PO_4 . Secondly, mineralization in intermediate and deep waters may be different for Cd, i.e. Cd input is relatively slower/faster than input of PO_4 . Thirdly, the mineralization in surface sediments (early diagenesis) may be more or less favourable for mobilization of Cd versus PO_4 . In coastal margin sediments early diagenesis leads to decoupled levels of Cd and phosphate (Gobeil et al., 1987). Decoupling of Cd and phosphate was found in the suboxic layer of the northwestern Indian Ocean (Saager et al., 1992) as a proxy for suboxic pore waters. On the other hand, deep-sea sediments generally are well oxygenated and diagenetic fluxes of Cd and phosphate deemed small (Klinkhammer et al., 1982; Jahnke et al., 1989).

From tracer distributions in the deep ocean one cannot distinguish between mineralization within ocean waters and mineralization in surficial sediments. For example, in-situ mineralization in the thermocline region may be augmented by lateral transport from a source in shelf and slope sediments at the ocean boundary. On the other hand, the depth distribution of tracers may serve as a guide for the depth distribution of the source function. Here, Boyle (1988) suggested that Cd is mineralized somewhat deeper than phosphate.

The most straightforward explanation would be that Cd is removed more efficiently from surface waters than phosphate. The settling biogenic matter would carry a high Cd/PO_4 signal, which upon mineralization would drive up the deep dissolved

Cd/PO₄-ratio. The depleted surface waters would retain a very low Cd/PO₄-ratio (Fig. 3). The excellent dataset recently reported (Sherrell, 1989) on particulate Cd concentrations in the northwest Atlantic and northeast Pacific Oceans appears consistent with this description, as is further outlined below.

Within the Atlantic Ocean, the Cd/PO₄-trends are modest at best. The deep Iceland–Greenland basin source waters carry very little Cd (~ 195 pM) and phosphate (~ 0.88 – 1.07 μ M) with an overall ratio of ($\sim 0.2 \times 10^{-3}$) (Table 2). In the northwest Atlantic Ocean the particulate Cd/PO₄ ratio of about 0.08×10^{-3} in the surface waters (Sherrell, 1989) exceeds the dissolved ratio of about 0.067×10^{-3} in surface waters. This hints at preferential removal of Cd, i.e. upon mineralization at depth the dissolved Cd/PO₄-ratio would be expected to increase. The dissolved ratio does increase with depth to about 0.23×10^{-3} in the North Atlantic Deep Water (Fig. 3), although the latter value barely exceeds the ratio of the deep Iceland–Greenland source waters. Absolute concentrations of Cd and PO₄ have, however, increased to about 286 pM and 1.27 μ M, respectively. The one South-Equatorial Atlantic station may again suggest higher levels of Cd (~ 385 pM) and PO₄ (~ 1.96 μ M), but the ratio is actually lower at 0.197×10^{-3} . Here, the paucity of South Atlantic data is felt. However, the Circumpolar Current shows a steep elevation of both absolute concentrations (Cd = 691–735 pM and PO₄ = 2.29–2.45 μ M) and Cd/PO₄-ratio (0.30×10^{-3}), the enhancements largely caused by the admixture of Weddell Sea derived water which carries high Cd and PO₄ contents (Fig. 7). Finally, the very high Cd/PO₄-ratios of 1.0 – 1.5×10^{-3} reported for particles in northeast Pacific surface waters would, upon deeper mineralization, be able to further enhance the Cd/PO₄-signal to the typical deep North Pacific ratio of about 0.33×10^{-3} at absolute concentrations of Cd = ~ 900 – 1100 pM and PO₄ = ~ 2.9 – 3.2 μ M.

The above interpretation needs further investigation, most notably the underlying chemical mechanism needs to be resolved. Nevertheless, the apparent fractionation of Cd versus PO₄ resem-

bles the preferential biogeochemical removal of ¹²C versus ¹³C from surface waters being the better understood cause of the also more accurately documented deep water distribution of the isotopic ratio ¹²C/¹³C (better known as ¹³C/¹²C). Obviously the analogy is imperfect. The ¹³C/¹²C ratio is also affected by air–sea gas exchange, whereas for Cd/PO₄ the underlying chemical mechanisms are not known and the dataset smaller with lower precision.

Saager and De Baar (1993) assessed the likelihood of the various mechanisms for fractionation of Cd and PO₄ with a metal–nutrient simulation model. In brief, they found that preferential removal of Cd by biota in surface waters leads to better resemblance to the oceanic distributions of Cd and PO₄ and also yields the significant negative Cd intercept at PO₄ = 0 in the global deep water relationship (e.g. Eq. 6 for dotted line in Fig. 4). This appears consistent with the findings for the couple Ge/Si which in itself represents the opposite case of Cd/PO₄. Here, Froelich et al. (1989), following Murnane and Stallard (1988), invoked discrimination against Ge during removal from surface waters for consistency with the observed positive Ge intercept at Si = 0 in the global relationship. Alternatively, Saager and De Baar (1993) also explored the deeper regeneration scenario for Cd as proposed by Boyle (1988). Briefly, this also yields a reasonable, but slightly less adequate fit to the oceanic distributions. For the deep water ($> \sim 1000$ m) at each given station this would lead to an increase of the Cd/PO₄-ratio with depth, analogous to the increasing Si/PO₄-ratio with depth, hinting at deeper regeneration of silicate versus phosphate. However, for all stations we hardly ever found the deep Cd/PO₄-ratio increasing with depth (the stations off New Zealand of Hunter and Ho, 1991 being the notable exception). At almost all individual stations, the Cd/PO₄-ratio in the deep water (> 1000 m) is constant with depth; only by comparing deep stations we did find an increase with time (age).

Summarizing oceanic fractionation of Cd and PO₄ is a prerequisite for realistic model simulations. Fractionation during uptake appears more convincing when comparing the admittedly small oceanic dataset (this work) with a simple model

(Saager and De Baar, 1993). Fractionated mineralization of Cd at greater depth is not entirely consistent with the field data, but cannot be ruled out either since we realize that the model is not yet fully constrained due to the very small Cd-PO₄ dataset.

The only other way to maintain distinct differences between ocean basins would be by relying on very different overall oceanic residence times of Cd and phosphate, with both residence times also to be in the same order as the interoceanic mixing time (500–1500 yr). However, the overall oceanic residence times of phosphate and Cd are long compared to interoceanic exchange, and at similar regeneration depths the distributions would have to be, and indeed are, quite similar (as is also the case for nitrate versus phosphate). For phosphate, the oceanic residence time is in the order of 100,000 yr. Depending on the selected rate term (e.g. river input, scavenging removal) and its chosen value the residence time estimates of Cd range from 18,000 to 177,800 yr (Balistrieri et al., 1981; Martin and Whitfield, 1983; Boyle, 1988).

After all, the Cd/PO₄-ratio in surface waters is almost always lower than in underlying thermocline and deep waters (Fig. 3). The very low Cd/PO₄-ratio of about 0.16×10^{-3} in coastal waters off Oman (Table 1) at the peak of the upwelling season is well below the ratio ($0.305 - 0.388 \times 10^{-3}$) in the underlying source waters (Table 2), indicative also of efficient stripping of Cd out of the surface waters. Summarizing, our proposed hypothesis of preferential removal of Cd from surface waters appears best in keeping with the currently available, limited, global dataset.

There are also some independent lines of evidence supporting Cd/PO₄ fractionation in surface waters (albeit not necessarily pointing at higher Cd/PO₄ in particles). Kremling and Pohl (1990) reported very different Cd/PO₄ ratios for summer and winter in northeast Atlantic surface water sections, implying seasonal variation in the removal and regeneration of Cd versus phosphate. On the other hand, the corresponding data for phosphate and nitrate were tightly coupled (Kremling and Pohl, 1990). In culture experiments it was shown that Cd-PO₄ removal from seawater is dependent on the plankton species as well as on the existing

Cd/PO₄ relation in the euphotic zone (Abe and Matsunagu, 1988). Finally, recent laboratory studies provided evidence towards biochemical substitution of Cd for Zn in marine diatoms at very low ambient Zn activities (Price and Morel, 1990). Whether or not this also applies to other marine algae is not yet evident. Also, variations of ambient Zn levels and speciation (Donat and Bruland, 1990) would exert a major control. Implications for the field are therefore not certain. Yet, the overall impact of this truly biochemical role of Cd on its large scale geochemical cycling would be less consistent than for the absolutely essential, hence more tightly coupled, nitrate and phosphate (Fanning, 1992).

7. The present as a key to the past?

One major reason for studying the modern relationship between Cd and PO₄ is its crucial role in interpretation of a paleoceanographic tracer. Throughout the past decade evidence was found in the sedimentary record for distinct links between shifts of the Cd/Ca elemental ratio in fossil shells of mostly benthic foraminifera, with shifts in the isotopic signatures ¹³C/¹²C and ¹⁸O/¹⁶O of the same shell material (Boyle and Keigwin, 1982, 1985, 1987; Boyle, 1988). This intriguing record of the Cd/Ca-ratio may serve as a paleoceanographic tracer, e.g. for paleo-Cd or paleocirculation. This application hinges on at least one inherent requirement:

(1) The distribution coefficient of Cd between seawater and foraminifera shells is uniform and well-defined

In addition, the Cd/Ca-record has often been interpreted as a proxy for paleoceanographic distributions of the nutrients, notably phosphate (Boyle, 1986, 1990; Curry et al., 1988; Duplessy et al., 1988; Broecker and Denton, 1989; Duplessy and Labeyrie, 1989; Lea and Boyle, 1989, 1990; Delaney, 1990). Presumably fossil shells can be used to infer nutrient distributions in ancient oceans (Boyle, 1988). Latter application hinges on the above as well as a second inherent requirement:

(II) The seawater ratio of Cd/PO₄ is constant throughout the world ocean and throughout geological time

It is noted that the modern oceanic relation of Cd–PO₄ has been applied incorrectly as evidence in support of both requirements (I) and (II) simultaneously. Below we will unravel this matter by first (section 7.1) looking at requirement (II) and then (section 7.2) at requirement (I). Recommendations are given for the correct route for validation of both requirements.

7.1 The seawater ratio

The previous sections 1–6 all underline the concept of the deep Cd/PO₄-ratio increasing with age of the water mass. Obviously, this implies that the general oceanic circulation as it exists today is crucial for the modern distribution of the Cd/PO₄-ratio. Most likely, this paradigm holds throughout geological time, i.e. at periods with different circulation, the resulting distribution of the Cd/PO₄-ratio would also be different. For example, during a glacial period the (partial) cessation of North Atlantic deep water formation (Broecker and Denton, 1989) would reduce deep circulation and the average age of the deep water may well have been about twice that of today (Shackleton et al., 1988).

Conceivably, the deep Cd/PO₄-ratio would in general also have been different during a glacial period (Fig. 4). Also, the often suggested higher biological productivity during a glacial period would further enhance the surface ocean fractionation of Cd versus PO₄, i.e. further enhance the shift of the deep water Cd/PO₄-ratio. These hypotheses were recently tested with a multibox model, where it was shown that during a glacial the deep water Cd/PO₄ ratios of different ocean basins tend to merge to a much narrower range than in the current interglacial (Saager and De Baar, 1993). Hence, it is virtually inevitable that the Cd/PO₄-ratio shifts with shifts in circulation, i.e. the global relation between Cd and phosphate not only varies in space but also in time. All evidence points at significant variations throughout for example the Phanerozoic. The analogy of Cd/PO₄ with ¹²C/¹³C appears relevant also in the time domain.

7.2 The distribution coefficient of Cd

The Cd/Ca-ratio within the crystal lattice of the calcite foraminifera shells is expected to be linearly related to the Cd/Ca-ratio in bottom waters:

$$(Cd/Ca)_{\text{foram}} = D' (Cd/Ca)_{\text{sw}} \quad (13)$$

where D' is an apparent coefficient of distribution. For seawater we may write:

$$(Cd/Ca)_{\text{sw}} = [(Cd/PO_4)_{\text{sw}} \cdot (1/Ca)_{\text{sw}}] \cdot (PO_4)_{\text{sw}} \quad (14)$$

and by combination with the former Eq. (13) one arrives at:

$$(Cd/Ca)_{\text{foram}} = [D' \cdot (Cd/PO_4)_{\text{sw}} \cdot (1/Ca)_{\text{sw}}] \cdot (PO_4)_{\text{sw}} = [B] \times (PO_4)_{\text{sw}} \quad (15)$$

where $[B]$ is a factor ideally uniform in space and time. Obviously, the three factors of which $[B]$ consists need to be independently quantified. Latter requirement of mutual independence has often been ignored.

The term $(1/Ca)$ is straightforward and calculated from the Ca²⁺-ion concentration in seawater which is proportional to salinity. This can easily be done but has thus far been deemed trivial: the oceanic variation of salinity is relatively small and here we will assume that $[Ca^{2+}]$ is constant at 10.27 mMol/kg for assumed salinity of 35. Given the typical oceanic range of about 33–37 the error would only be about 6%, i.e. a relatively small error which in the future can easily be remedied.

The (Cd/PO₄) ratio is the principal subject of our study. For the modern ocean we found that neither one of the set of relationships (4) and (5) has a zero intercept; as a result the Cd/PO₄ ratio increases with increasing PO₄, i.e. is not constant in place. Hence, the covariation is non-ideal and would tend to vary over geological time scales (section 7.1).

Indirect assessments of D' have been reported from Atlantic and Pacific core tops (Hester and Boyle, 1982; Boyle, 1988), but suffer from the fact that they are depending on the seawater relationship between Cd and PO₄. In other words two of the three factors within the parameter $[B]$ of Eq. (15) are in fact interdependent i.e. incorrect.

Table 3

The distribution coefficients D' of pelagic forams assessed directly (Delaney, 1989) by ^{109}Cd radiotracer techniques. Also listed the values derived from comparison between measured Cd/Ca in benthic forams and calculated Cd/Ca in seawater, the latter derived from given seawater relations (1) and (2) of Cd/PO_4 at given seawater Ca concentration. The error of D' is listed as standard deviation, or as r when D' was assessed by linear regression. When presumably some value was used but not reported we list (–). For comparison our best estimates of the global seawater Cd/PO_4 relation

Author	D'	SD of D' (or r)	Seawater relation $\text{Cd}[\text{nM}] = a\text{P}[\mu\text{M}] + b$			(Ca)seaw. (at $S = 35$ [mmol])
			a	$b[\text{nM}]$	r	
Delaney (1989) (pelagic)	2–4	(direct with Cd radiotracer)			–	–
<i>Comparison</i>						
Hester and Boyle (1982)	2.0	0.4	–	–	–	–
as per Boyle (1988)	2.0	0.4	0.35	zero	–	–
we calculate	1.87	($r = 0.84$)	0.35	zero	–	10.27
Boyle (1988)						
for $\text{PO}_4 > 1.3 \mu\text{M}$	2.9	> 0.6	0.40	–0.25	–	–
for $\text{PO}_4 < 1.3 \mu\text{M}$	2.9	> 0.6	0.21	zero	–	–
we calculate	2.58	($r = 0.98$)	as above (Boyle 1988)			10.27
<i>This work</i>						
select (SD < 10%) deep	all PO_4 -values		0.413	–0.259	0.98	(10.27)
for $\text{PO}_4 > 2\mu\text{M}$			0.375	–0.145	0.85	(10.27)
for $\text{PO}_4 < 2\mu\text{M}$			0.148	0.065	0.74	(10.27)
only bottom waters			0.388	–0.190	0.88	(10.27)

Apparently the relationships (1) and (2) for Cd versus PO_4 in seawater were used to convert the actually measured PO_4 into an estimated seawater Cd which was then plotted versus Cd/Ca in forams (Boyle, 1988, fig. 3) for which we then reconstruct (at $\text{Ca}^{2+} = 10.27 \text{ mM}$):

$$(\text{Cd}/\text{Ca})_{\text{foram}} = 0.0037 + 2.58(\text{Cd}/\text{Ca})_{\text{sw}} \quad (r = 0.98) \quad (16)$$

where the apparent $D' = 2.58$ at virtually zero-off-set does not deviate significantly from $D' = 2.9 \pm 0.6$ derived from a histogram (Boyle, 1988) rather than by regression. However, when properly taking into account the error in predictability of seawater Cd from seawater phosphate (Fig. 4), the derived D' -values would in fact have a far wider range than the ± 0.6 suggested previously (Boyle, 1988). Recently, the distribution coefficient D' has been assessed independently from the uptake of Cd-radiotracer into calcite shells and was found to be in the range of $2 < D < 4$ for pelagic (rather than benthic) foraminifera (Delaney, 1989), where the

relative error is significant when compared with the signal of the Cd/Ca record (e.g. Boyle and Keigwin, 1982, 1985, 1987). This and the below assessments are summarized in Table 3.

More recently, Boyle (1992) suggested, on the basis of an overview of global core tops Cd/Ca data, that the D' -values were depth-dependent. Unfortunately, this treatise also suffers from the fact that D' appears to be calculated on the basis of assumed oceanic $\text{Cd}-\text{PO}_4$ relationships, the same circular argument as mentioned in the previous paragraph (Boyle, 1992, fig. 3, where method for “Estimated Bottom Water Cd, nmol/kg” cannot be found in the text but is presumably based on actually measured phosphate and above relationships 1 and 2). In addition to being a function of depth, it appears that D' may also vary from basin to basin (Saager and De Baar, 1993). These and other considerations led Saager and De Baar (1993) to point at the risks of using an improperly defined D' to quantitatively interpret the Cd/Ca record.

Obviously an independent assessment of D' , as

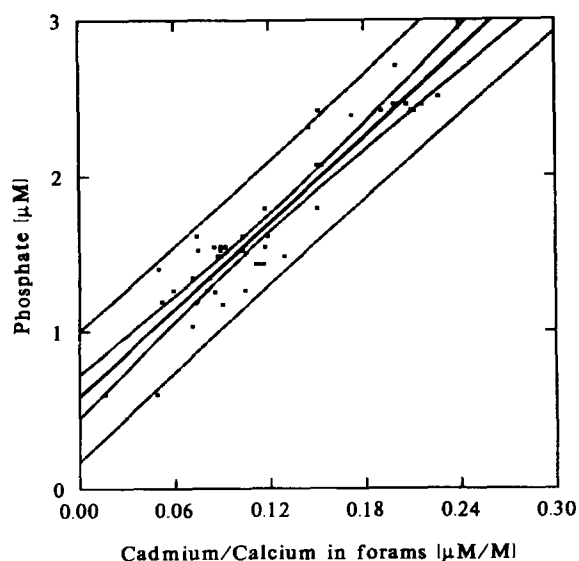


Fig. 8. The relation between Cd/Ca in benthic foraminifera of selected core tops with the ambient concentration of bottom water phosphate, data from table 1 of (Boyle, 1988). Linear regression (middle line) with 95% confidence interval (inner curves). Predictability interval (outer lines) at 95% confidence level for predicting the band width of phosphate in the modern ocean from a given discrete value of Cd/Ca. The range of predictability is strongly depending on the ranges of predictability of dissolved phosphate from given dissolved Cd; the latter plot is omitted as it is virtually identical to the inverse of Fig. 4.

well as better overall insight in the relation (15) for the modern ocean is required and may likely be achieved either experimentally (after Delaney, 1989) or by simultaneous measurements of (1) $(\text{Cd}/\text{Ca})_{\text{foram}}$ in core top foraminifera and the concentrations of (2) dissolved Cd, (3) phosphate as well as (4) salinity of the corresponding bottom water (preferably also in several ocean basins). This would allow the paleoceanographic reconstruction of Cd in seawater which may prove very useful in combination with other paleoceanographic tracers ($^{18}\text{O}/^{16}\text{O}$; $^{13}\text{C}/^{12}\text{C}$).

7.3 Cd/Ca in forams as an indicator of phosphate

The overall relation (15) may be derived directly from the primary data of Cd/Ca in benthic shells of selected core tops with well-documented continuous sedimentation (Boyle, 1988) and bottom

water phosphate:

$$(\text{Cd}/\text{Ca})_{\text{foram}} = -0.059 + 0.101 \times (\text{PO}_4) \quad (r = 0.98) \quad (17)$$

This relationship (Fig. 8) is impressive but not an ideal covariation due to its significant non-zero intercept. For a given modern Cd/Ca value the modern phosphate can be predicted within a band width of about $\pm 0.4 \mu\text{M}$ at the 95% confidence level. This band width (i.e. the error of the overall factor B) can largely be ascribed to the band widths for the predictability of the seawater Cd/ PO_4 -ratio in Eq. (15), judging from predictability ranges shown in Fig. 4.

Here, a conceivable caveat is due to the depth of habitat of benthic foraminifera in relation to the ambient concentrations of Cd and phosphate in bottom waters or sedimentary pore waters, respectively. For example, Mackensen and Douglas (1989) showed that from several different species only one truly epibenthic species (*P. ariminensis*) should be used to infer bottom water paleochemistry. Many foraminifera show a maximum abundance at 1–4 cm within the sediments (Corliss and Emerson, 1990). Decoupling of Cd and phosphate during early diagenesis was already mentioned above (Gobeil et al., 1987; Saager et al., 1992). Recently, similar concern was expressed with regards to observed decoupling of Cd and $\delta^{13}\text{C}$ in coastal margin sediments (McCorkle and Klinkhammer, 1991).

7.4 Summary

Upon correct determination of D' the reconstruction of paleo-Cd is feasible. This in turn, has been suggested as a proxy for the paleoceanographic distribution of phosphate. Here, the modern relationship (17) between $(\text{Cd}/\text{Ca})_{\text{forams}}$ and phosphate in the modern ocean at first glance may look promising (Fig. 8). However, the full Eq. (15) and its underlying relationship(s) (Eqs. 4 and 5, or combined Eq. 6) between Cd and PO_4 in seawater are not constant but vary in space, hence inevitably also in time. The latter time-shifts of the oceanic distribution of the Cd/ PO_4 -ratio were demonstrated by ocean modeling (Saager and De

Baar, 1993). Intensity of these time shifts is significant in comparison with the strength of the fossil Cd/Ca signal, hence affects the feasibility of the Cd/Ca record as independent tracer of nutrient distributions in ancient oceans. Truly isotopic tracers may be more suitable, some of these are known to have some bearing on ($^{13}\text{C}/^{12}\text{C}$) or potential for ($^{15}\text{N}/^{14}\text{N}$; Altabet and Curry, 1989) reconstruction of paleonutrients.

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Note added in proof

The recently reported observations in the Indian Ocean of Morley et al. (1993) are consistent with the current findings. Briefly their deep water values of Cd and PO_4 would increase the number of points in the lower end of the Antarctic/Indo/Pacific cluster of our Fig. 4, hence lead to minor adjustments in the relationships 4, 5 and 6.

References

- Abe, K. and Matsanagu, K., 1988. Mechanism controlling Cd and PO_4 concentrations in Funka Bay, Japan. *Mar. Chem.*, 23: 145–152.
- Altabet, M.A. and Curry, W.B., 1989. Testing models of past ocean chemistry using foraminiferal $^{15}\text{N}/^{14}\text{N}$. *Global Biogeochem. Cycles*, 3: 107–119.
- Balistreri, L., Brewer, P.G. and Murray, J.W., 1981. Scavenging residence times of trace metals and surface chemistry of sinking particles in the deep sea. *Deep-Sea Res.*, 28: 101–121.
- Bordin, G., Appriou, P. and Tréguer, P., 1987. Répartitions horizontale et verticale du cuivre, du manganèse et du cadmium dans le secteur indien de l'Océan Antarctique. *Oceanol. Acta*, 10: 411–420.
- Boyle, E.A., 1986. Paired carbon isotope and cadmium data from benthic foraminifera: implications for changes in deep ocean P and atmospheric carbon dioxide. *Geochim. Cosmochim. Acta*, 50: 265–276.
- Boyle, E.A. 1988. Cadmium: chemical tracer of deepwater paleoceanography. *Paleoceanography*, 3(4): 471–489.
- Boyle, E.A., 1990. Quaternary deep water oceanography. *Science*, 249: 863–870.
- Boyle, E.A., 1992. Cadmium and $\delta^{13}\text{C}$ paleochemical ocean distributions during the stage 2 glacial maximum. *Annu. Rev. Earth Planet. Sci.*, 20: 245–287.
- Boyle, E.A. and Keigwin, L.D., 1982. Deep circulation of the North Atlantic over the last 200,000 years: geochemical evidence. *Science*, 218: 784–787.
- Boyle, E.A. and Keigwin, L.D., 1985. Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: changes in deep ocean circulation and chemical inventories. *Earth Planet. Sci. Lett.*, 76: 135–150.
- Boyle, E.A. and Keigwin, L.D., 1987. North Atlantic thermohaline circulation during the past 20,000 years linked to high-latitude surface temperature. *Nature*, 330: 35–40.
- Boyle, E.A., Sclater, F.R. and Edmond, J.M., 1976. On the marine geochemistry of cadmium. *Nature* 263: 42–44.
- Boyle, E.A., Huested, S.S. and Jones, S.P., 1981. On the distribution of copper, nickel, and cadmium in the surface waters of the North Atlantic and North Pacific Ocean. *J. Geophys. Res.*, 86: 8048–8066.
- Boyle, E.A., Reid, D.F., Huested, S.S. and Hering, J., 1984. Trace metals and radium in the Gulf of Mexico: an evaluation of river and continental sources. *Earth. Planet. Sci. Lett.*, 69: 69–87.
- Boyle, E.A., Chapnick, S.D., Bai, X.X. and Spivack, A., 1985. Trace metal enrichments in the Mediterranean Sea. *Earth Planet. Sci. Lett.*, 74: 405–419.
- Broecker, W.S. and Denton, G.H., 1989. The role of ocean-atmosphere reorganizations in glacial cycles. *Geochim. Cosmochim. Acta*, 53: 2465–2501.
- Broecker, W.S., Takahashi, T. and Takahashi, T., 1985. Sources and flow patterns of deep-ocean waters as deduced from potential temperature, salinity and initial phosphate concentration. *J. Geophys. Res.*, 90: 6925–6939.
- Bruland, K.W. 1980. Oceanographic distributions of cadmium, zinc, nickel and copper in the north Pacific. *Earth Planet. Sci. Lett.*, 47: 176–198.
- Bruland, K.W., 1983. Trace elements in seawater. In: J.P. Riley and R. Chester (Editors), *Chemical Oceanography*, 8. Academic, London, pp. 157–220.

- Bruland, K.W. and Franks, R.P., 1983. Manganese, nickel, copper, zinc and cadmium in the western north Atlantic. In: C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg (Editors), *Trace Metals in Sea Water*. Plenum, New York, NY, pp. 395–414.
- Bruland, K.W., Knauer, G.A. and Martin, J.H., 1978. Cadmium in northeast Pacific waters. *Limnol. Oceanogr.*, 23: 618–625.
- Corliss, B.H. and Emerson, S., 1990. Distribution of Rose bengal stained deep-sea benthic foraminifera from the Nova Scotian continental margin and Gulf of Maine. *Deep-Sea Res.*, 37: 381–400.
- Curry, W.B., Duplessy, J.-C., Labeyrie, L.D. and Shackleton, N.J., 1988. Changes in the distribution of $\delta^{13}\text{C}$ of deep water CO_2 between the last glaciation and the Holocene. *Paleoceanography*, 3: 317–342.
- Danielsson, L.G. and Westerlund, S., 1983. Trace metals in the Arctic Ocean. In: C.S. Wong, E.A. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg (Editors), *Trace Metals in Seawater*. Plenum, New York, NY, pp. 85–96.
- Danielsson, L.G., Magnusson, B. and Westerlund, S., 1985. Cadmium, copper, iron, nickel and zinc in the northeast Atlantic Ocean. *Mar. Chem.*, 17: 23–41.
- De Baar, H.J.W., Schijf, J. and Byrne, R.F., 1991. Solution chemistry of the rare earth elements in seawater. *Eur. J. Solid State Inorg. Chem.*, 28: 357–374.
- Delaney, M.L. 1989. Uptake of cadmium into calcite shells by planktonic foraminifera. *Chem. Geol.*, 78: 159–165.
- Delaney, M.L. 1990. Miocene benthic foraminiferal Cd/Ca records: South Atlantic and Western Equatorial Pacific. *Paleoceanography*, 5: 743–760.
- Donat, J.R. and Bruland, K.W., 1990. A comparison of two voltammetric techniques for determining zinc speciation in northeast Pacific Ocean waters. *Mar. Chem.*, 28: 301–323.
- Duplessy, J.-C., Shackleton, N.J., Fairbanks, R.G., Labeyrie, L., Oppo, D. and Kallel, N., 1988. Deepwater source variations during the last climatic cycle and their impact on the global deepwater circulation. *Paleoceanography*, 3: 343–360.
- Duplessy, J.-C. and Labeyrie, L., 1989. Global ocean circulation during the last Ice Age: Enhanced intermediate water formation and reduced deep water circulation. In: A. Ayala-Castanares, W. Wooster and A. Yanez-Arancibia (Editors), *Oceanography*, 1988, pp. 81–85.
- Fanning, K.A. 1992. Nutrient provinces in the sea: concentration ratios, reaction rate ratios and ideal covariation. *J. Geophys. Res.*, 97: 5693–5712.
- Frew, R.D. and Hunter, K.A., 1992. Influence of Southern Ocean waters on the cadmium–phosphate properties of the global ocean. *Nature*, 360: 144–146.
- Froelich, P.N., Mortlock, R.A. and Shemesh, A. 1989. Inorganic Germanium and Silica in the Indian Ocean: biological fractionation during $(\text{Ge/Si})_{\text{opal}}$ formation. *Global Biogeochem. Cycles*, 3(1): 79–88.
- Gobeil, C., Silverberg, N., Sundby, B. and Cossa, D., 1987. Cadmium diagenesis in Laurentian trough sediments. *Geochim. Cosmochim. Acta*, 51: 589–596.
- Hester, K. and Boyle, E., 1982. Water chemistry control of cadmium content in Recent benthic foraminifera. *Nature*, 298: 260–261.
- Hunter, K.A. and Ho, F.W.T., 1991. Phosphorus–cadmium cycling in the northeast Tasman Sea, 35–40°S. *Mar. Chem.*, 33: 279–298.
- Jahnke, R.A., Emerson, S.R., Reimers, C.E., Schuffert, J., Ruttenberg, K. and Archer, D., 1989. Benthic recycling of biogenic debris in the eastern tropical Atlantic Ocean. *Geochim. Cosmochim. Acta*, 53: 2947–2960.
- Jones, C.J. and Murray, J.W., 1984. Nickel, cadmium and copper in the northeast Pacific off the coast of Washington. *Limnol. Oceanogr.*, 29: 711–720.
- Klinkhammer, G., Heggie, D.T. and Graham, D.W., 1982. Metal diagenesis in oxic marine sediments. *Earth Planet. Sci. Lett.*, 61: 211–219.
- Knauer, G.A. and Martin, J.H., 1981. Phosphorus–cadmium cycling in northeast Pacific waters. *J. Mar. Res.*, 39: 65–78.
- Kremling, K. and Pohl, C., 1990. Studies on the spatial and seasonal variability of dissolved cadmium, copper and nickel in northeast Atlantic surface waters. *Mar. Chem.*, 27: 43–60.
- Lea, D.W. and Boyle, E.A., 1989. A 210,000-year record of barium variability in the deep northwest Atlantic Ocean. *Nature*, 347: 269–272.
- Lea, D.W. and Boyle, E.A., 1990. Foraminiferal reconstructions of barium distributions in water masses of the glacial oceans. *Paleoceanography*, 5: 719–742.
- Mackensen, A. and Douglas, R.G., 1989. Down-core distribution of live and dead deep-water borderland. *Deep-Sea Res.*, 36: 879–900.
- Martin, J.M. and Whitfield, M., 1983. River input of chemical elements to the ocean. In: C.S. Wong, E.A. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg (Editors), *Trace Metals in Seawater*. Plenum, New York, NY, pp. 265–296.
- Martin, J.H., Bruland, K.W. and Broenkow W.W., 1976. Cadmium transport in the California Current. In: H. Windom and R. Duce (Editors), *Marine Pollutant Transfer*. Heath, Lexington, MA, pp. 159–184.
- Martin, J.H., Gordon, R.M. and Fitzwater, S.E., 1990. Iron in Antarctic waters. *Nature*, 345: 156–158.
- Martin, J.H., Knauer, G.A. and Broenkow, W.W., 1985. VERTEX: the lateral transport of manganese in the northeast Pacific. *Deep-Sea Res.*, 32: 1405–1427.
- Martin, J.H., Gordon, R.M., Fitzwater, S.E. and Broenkow, W.W., 1989. VERTEX: Phytoplankton/iron studies in the Gulf of Alaska. *Deep-Sea Res.*, 35: 649–680.
- Matsunaga, K. and Abe, K., 1985. Relationship between cadmium and phosphate in the northwest Pacific Ocean. *J. Oceanogr. Soc. Jpn.*, 41: 183–187.
- Morley, N.H., Statham, P.J. and Burton, J.D., 1993. Dissolved trace metals in the southwestern Indian Ocean. *Deep-Sea Res.*, 40: 1043–1062.
- Murnane, R.G. and Stallard, R.F., 1988. Germanium/silicon fractionation during biogenic opal formation. *Paleoceanography*, 3: 461–469.
- McCorkle, D. and Klinkhammer, G.P., 1991. Porewater cad-

- mium geochemistry and the porewater cadmium: $\delta^{13}\text{C}$ relationship. *Geochim. Cosmochim. Acta*, 55: 161–168.
- Nolting, R.F., de Baar, H.J.W. and Duinker, J.C., 1987. Trace metals Ni, Cu and Cd in waters around Iceland. *EOS Trans. Am. Geophys. Union*, 68: 66.
- Nolting, R.F., Hutagalung, H. and Moeliyadi Moelyo, D., 1989. Snellius II Expedition: results of the investigation on metals, phosphate and silicate. *Neth. Inst. Sea Res. Techn. Rep.* 89/4, 118 pp.
- Nolting, R.F., De Baar, H.J.W., Masson, A. and Van Bennekom, A.J., 1991. Cadmium, copper and iron in the Weddell Sea and Weddell/Scotia Confluence (Antarctic). *Mar. Chem.*, 35: 219–243.
- Olafsson, J., 1983. Mercury concentrations in the north Atlantic in relation to cadmium, aluminium and oceanographic parameters. In: C.S. Wong, E.A. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg (Editors), *Trace Metals in Seawater*. Plenum, New York, NY, pp. 475–486.
- Orren, M.J. and Monteiro, P.M.S., 1985. Trace element geochemistry in the Southern Ocean. In: W.R. Siegfried, P.R. Condy and R.M. Laws (Editors), *Antarctic Nutrient Cycles and Food Webs*. Springer, Berlin, pp. 30–37.
- Ostlund, H.G., Craig, H., Broecker, W.S. and Spencer, D., 1987. *Geosecs, Atlantic, Pacific and Indian Ocean expeditions, Vol. 7: Shorebased Data and Graphics*. US Gov. Printing Off., Washington, DC, 200 pp..
- Price, N.M. and Morel, F.M.M., 1990. Cadmium and cobalt substitution for zinc in a marine diatom. *Nature*, 344: 658–660.
- Saager, P.M. and de Baar, H.J.W., 1993. Limitations to the quantitative application of Cd as a paleoceanographic tracer, based on results of a multi-box model (*MENU*) and statistical considerations. *Global Planet. Change*, 8: 69–92.
- Saager, P.M., De Baar, H.J.W. and Howland, R., 1992. Cd, Zn, Ni and Cu in the Indian Ocean. *Deep-Sea Res.*, 39(1): 9–35.
- Sakamoto-Arnold, C.M., Hanson Jr., A.K., Huizenga, D.L. and Kester, D.R., 1987. Spatial and temporal variability of cadmium in Gulf Stream warm-core rings and associated waters. *J. Mar. Res.*, 45: 201–230.
- Shackleton, N.J., Duplessy, J.C., Arnold, M., Maurice, P., Hall, M.A. and Cartledge, J., 1988. Radiocarbon age of last glacial Pacific deep water. *Nature*, 335: 708–711.
- Sherrell, R.M., 1989. *The Trace Metal Geochemistry of Suspended Oceanic Particulate Matter*. Ph.D. Thesis. WHOI/MIT Oceanogr., 211 pp.
- Statham, P.J., 1994. Ph.D. thesis. Univ. Southampton, Southampton.
- Statham, P.J., Burton, J.D. and Hydes, D.J., 1985. Cd and Mn in the Alboran Sea and adjacent North Atlantic: geochemical implications for the Mediterranean. *Nature*, 313: 565–567.
- Westerlund, S. and Öhman, P., 1991. Cadmium, copper, cobalt, nickel, lead and zinc in the water column of the Weddell Sea. *Geochim. Cosmochim. Acta*, 55: 2127–2146.
- Yeats, P.A. and Campbell, J.A., 1983. Nickel, copper, cadmium and zinc in the northwest Atlantic Ocean. *Mar. Chem.* 12: 43–58.
- Yeats, P.A. and Westerlund, S., 1991. Trace metal distributions at an Arctic Ocean ice island. *Mar. Chem.*, 33: 261–277.